



Upcycling of polyvinyl chloride to hydrocarbon waxes via dechlorination and catalytic hydrogenation

Scott Svadlenak^a, Sophie Wojcik^a, Oluwafemi Ogunlalu^b, Makayla Vu^a, Maoz Dor^a, Bryan W. Boudouris^{b,c}, Dorte Wildenschild^a, Konstantinos A. Goulas^{a,*}

^a School of Chemical, Biological and Environmental Engineering, Oregon State University, 105 SW 26th St, Corvallis, OR 97331, USA

^b Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907, USA

^c Charles D. Davidson School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907, USA

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ABSTRACT

Converting polymer waste to marketable products is a promising method to incentivize the development of competitive waste upcycling processes. Polyvinyl chloride (PVC) waste streams pose a unique challenge in this regard because of the presence of Cl atoms in the molecule. To address this issue, we report here a method to upcycle PVC plastics and produce a polyethylene wax in a mixed amine-water system, using hydrogen and a heterogeneous catalyst. We demonstrate that alkylamines as homogeneous catalysts and as Cl⁻ sequestration media successfully dechlorinate PVC to a polyene, which is hydrogenated over a Pt/C heterogeneous catalyst. At optimal conditions, hydrocarbon wax yields greater than 70 % with melt temperatures above 80 °C were achieved. We use X-ray tomography to illustrate the PVC dissolution and reaction and quantify the product by differential scanning calorimetry (DSC). Characterization of the product reveals complete dechlorination and hydrogenation, as well as partial C-C bond scission, indicating a product similar to polyolefin adhesive waxes.

1. Introduction

The accumulation of waste plastic in the environment and in communities around the world is a central issue in the engineering, science, and policy of solid waste management, with millions of tons of plastic entering waste streams every year [1]. Recent efforts in the polymer chemical recycling field have demonstrated the feasibility of converting waste polyolefin plastics to useful fuels and chemicals [2–4]. For example, hydrogenolysis is a promising effective catalytic process to convert waste polyolefins into liquid hydrocarbons [5–7]. One of the most abundant polymers in waste plastics streams, making up 7 % of waste plastic entering the environment every year [1], polyvinyl chloride (PVC), is commonly found in commingled plastics streams [8]. Despite PVC abundance worldwide, mechanical recycling rates for PVC plastics are very low due to substantial economic barriers [9,10]. Alternative recycling processes at high temperatures that convert waste-to-energy are complicated by the addition of PVC due to the high chlorine presence in the polymer which results in the production of toxic chlorinated hydrocarbons and HCl [11,12]. These challenges result in the landfilling of virtually all PVC produced [9]. Furthermore, circular

economy policies such as the proposed Break Free from Plastics Pollution Act and the implemented European End of Life Vehicles Directive provide strong incentives to develop new technologies to chemically recycle PVC-containing waste [13,14]. Further, waste polymer conversion in catalytic processes, such as hydrogenolysis, is demonstrably suppressed in feedstocks that contain PVC due to the high Cl presence [5]. While there exist hydrothermal processes to dechlorinate PVC, they do not convert PVC to valuable products, limiting their economic potential [15]. Some recent efforts have reported success in converting PVC to upcycled molecules and polymers [16,17].

There is significant academic interest in the dechlorination of chlorinated waste species [18–20]. Further, the removal of Cl atoms from waste PVC at moderate reaction temperatures has been explored in several papers. Poerschmann et al. showed that PVC can be effectively dechlorinated and converted to hydrochar at low temperatures in aqueous solvents with very little C-C bond cleavage or formation of toxic low molecular weight chlorinated hydrocarbons [15]. Meanwhile, the introduction of NaOH in low-temperature treatment of PVC can promote the formation of OH groups via nucleophilic substitution replacing the Cl atoms with OH on the polymer backbone [21]. The addition of bases

* Corresponding author.

E-mail address: kostas.goulas@oregonstate.edu (K.A. Goulas).

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may sequester released chlorine upon PVC dechlorination and the rate of dehydrochlorination of PVC was found to accelerate in basic solvents [22,23]. In hydrothermal dechlorination of PVC in neutral water, the generated HCl has been claimed to have an autocatalytic effect on the dechlorination of PVC [24]. However, the acidic conditions result in the formation of carbon black, which has residual chlorine and poor reusability. In these hydrothermal systems, the formation of polyene structures in the dechlorinated PVC chain are attributed to termination reactions that result in the incomplete dechlorination of the polymer as it converts to hydrochar [25].

Pioneering work by Keane demonstrated how introducing hydrogen and catalyst into a PVC hydrodechlorination process enables hydrogenation of olefin products [12]. However, the proposed PVC treatment by Keane resulted in a diverse mixture of solids, liquids, and gases which complicates its industrial implementation.

These studies demonstrate that while hydrothermal or catalytic treatment of PVC can result in its dechlorination, there is a need for chlorine sequestration and hydrogenation of the reactive intermediates. Catalytic hydrogenation of polymers such as polystyrene and polybutadiene is well studied with heterogeneous catalysts such as Ni, Pd, and Rh [26]. Further, Pt catalysts are highly active for C-H activation in reactions with polymers and were previously reported for dehydrogenation activity of polyethylene by Ellis [27]. In hydrogenation reactions, hydrogenolytic cleavage may readily occur and Pt is highly active for hydrogenolysis of polymer waste [6,28].

The main objective of this study was to develop a heterogeneously catalyzed PVC dechlorination process to produce high-value high density polyethylene (HDPE) waxes, by dechlorinating PVC using a base and hydrogenating it over a heterogeneous catalyst. HDPE waxes find industrial applications in numerous products such as hot melt adhesives [29]. We posited that an aqueous base will enable the elimination of HCl from the PVC polymer backbone, with the resulting double bond being hydrogenated over a heterogeneous metal catalyst. This process can be described as an A→B→C series of reactions where “A” is PVC, “B” is a dechlorinated polyene and product “C” is a hydrogenated, polyethylene-like waxy macromolecule (Scheme 1).

Obtaining such high value waxes from a PVC dechlorination process requires high selectivity to two reactions. The first (A to B) is the dechlorination of PVC that preserves the polymer backbone as a polyene type macromolecule. In the dechlorination reaction the undesired reaction product is hydrochar which can readily form from such a reactive intermediate as polyene [15]. The second reaction (B to C) is the hydrogenation of the dechlorinated backbone to a paraffin wax or linear polyethylene-type polymer. Pt catalyst was utilized in this study for the catalytic hydrogenation step.

2. Materials and methods

2.1. Materials

PVC powder with a weightaverage molecular weight of 43,000 and ammonia solution (33 %) was purchased from Millipore Sigma. 5 % Pt/C with a 5 % loading by weight was obtained from Millipore Sigma. N,N – dimethyloctylamine, N,N-dimethylhexylamine, triethylamine, N,N – dimethylbutylamine, triethanolamine, N-methyl-N-octylamine, and

triethylamine were obtained from TCI America or Fischer Scientific and used without further purification. The n-docosane wax standard was obtained from Alfa Aesar and a polybutadiene standard with number average molecular weight (M_n) of 5000 was obtained from Millipore Sigma. Triethylammonium HCl was prepared by mixing HCl solution (Fisher Chemical) with triethylamine and drying the solution.

2.2. Methods

2.2.1. Reaction experiments

Experiments were performed in glass batch systems with 2 mL liquid volume, connected to a pressure manifold of approximately 20 mL total volume (Qlabtech). In typical experiments, 100 mg of PVC powder, 20 mg catalyst powder as received and 2 mL of an organic base or inorganic base solution (2.5 M in the case of inorganic base, while the concentration of organic base was based on the ratio of nitrogen from the base to chlorine from the PVC in specific experiments) were loaded into a glass tube. The manifold was pressurized with hydrogen gas to 6.5 bar pressure and placed into an aluminum block preheated to the reaction temperature (Fig. S1). Reaction tubes were agitated with magnetic stir bars at a 600 rpm stir rate.

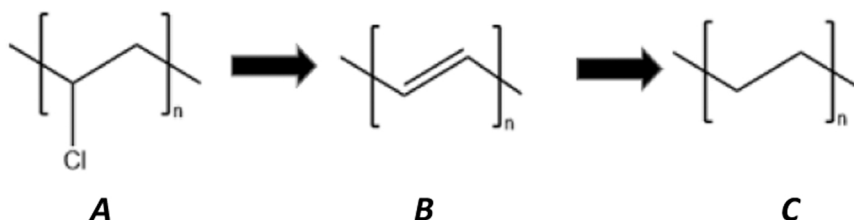
2.2.2. Reaction work up

Reaction work up was performed by cooling down the reaction tubes in room temperature water, the reaction product mixture of salt, catalyst, and polymer was then poured/scraped onto a crystallization dish and dried in a vacuum oven at 40 °C for 48 h. This dried product mixture was then used for analysis.

For some analyses the wax product is separated from the residual catalyst and salt from the reaction by drying in a vacuum oven to remove residual water and amine, then adding xylenes solvent and dissolving under stirring at 60 °C for 24 h. The solution is then added to water for salt/polymer separation and the aqueous and organic phases are separated via liquid-liquid extraction. Then, the organic phase is centrifuged to remove residual char and catalyst from the solution and the remaining organic solution is filtered and dried, obtaining product wax.

2.2.3. Product analysis

The heat of melting (ΔH_m) from Differential Scanning Calorimetry (DSC) analysis was measured as a function of the weight fraction of n-docosane wax in a matrix of triethylammonium HCl, Pt supported on carbon, and wax. Analysis of reaction product was performed with a TA instruments Q2000 DSC. A calibration curve generated from the plot of ΔH_m vs weight fraction wax (Fig. S2) was used to calculate the % wax yield for each product mixture. The ΔH_m for each product mixture was measured by integrating the melt curve on the resultant heating curve from DSC analysis. For heating curves where multiple melt temperatures are present, the weight average wax melt temperature is used and the sum of the heats of melting are used to calculate overall wax yield. An example of the heating curve for a reaction product mixture is shown in Fig. S3. Heating rates for the calibration curve and reaction analysis were 5 °C min⁻¹, however all samples were analyzed with two sequential heating curves, the first at 20 °C min⁻¹ and the second at 5 °C min⁻¹. This was done to confirm repeated melting and recrystallization behavior, as well as to ensure melt curve segregation if multiple heats of melting are



Scheme 1. Idealized series reaction converting PVC to polyene, which converts to HDPE.

observed.

To close the solids material balance the yield of char from the reaction was quantified with thermogravimetric analysis (TGA) using a TA instruments Q500 TGA. Data were collected at a heating rate of $2\text{ }^{\circ}\text{C min}^{-1}$ from ambient temperature to $700\text{ }^{\circ}\text{C}$ for a wet sample that was obtained directly from the reaction mixture. Nitrogen gas mixed with air with flow rates of 60 and 40 mL min^{-1} respectively were used for a sample mass of approximately 40 mg.

To close the gases material balance, the reaction tubes were cooled after reaction in a water ice bath while still connected to the reaction pressure manifold. The manifold system was connected to a line under vacuum which connected a 0.5 L Tedlar gas sample bag. The reaction tube system was then opened to allow gases to fill the Tedlar bag. 1 mL of Ar was injected into gas sample bags with reaction product gases and the Ar was used as an internal standard for gas chromatography (GC) analysis. GC analysis was performed with a Shimadzu GC-2014 instrument equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID). The column to the TCD detector was a Restek ShinCarbon ST (catalog # 80486-800) packed column while the column to the FID detector was an Agilent J&W HP-1 column (catalog # 19091Z-216).

The extent of polymer dechlorination and hydrogenation was measured by Fourier Transform Infrared Spectroscopy (FTIR) with a Thermo Scientific Nicolet 6700 FTIR. The analysis was performed with an Attenuated Total Reflectance (ATR) system in % transmittance mode. The FTIR spectra were collected from 600 to 3500 cm^{-1} . The C-Cl bond conversion was measured using peak area integration at $\sim 615\text{ cm}^{-1}$. Double bond character was measured by the increase/decrease of the C=C-H stretch peak area at $\sim 3000\text{--}3100\text{ cm}^{-1}$. The peak areas were normalized to the peak area of the C-H stretch at $\sim 2900\text{ cm}^{-1}$. A standard PVC sample for calibration of the dechlorination degree involved mixing pure PVC powder with Pt/C catalyst in appropriate masses to represent the reaction mixture, then mixing this sample with triethylamine for 24 h. and drying. After drying the PVC standard was analyzed with FTIR to obtain peak areas. Polybutadiene standard with number average molecular weight (M_n) = 5000 was analyzed with FTIR to obtain a calibration curve for the hydrogenation degree of the wax. Examples of the spectra of the product are shown in Figs. S4 and S5.

X-ray computed microtomography scans of the reaction mixtures were acquired at the microCT user facility at Oregon State University (<https://microct.oregonstate.edu>). In order to mount the samples, the content was transferred from a reaction tube to 3 mm NMR tubes (Wilmad). 1800 x-ray projections were acquired in a helical trajectory at 100 kV tube voltage, 40 μA tube current with 0.5 s exposure time, 0.8 mm aluminum filter, and resulted in a voxel resolution of $3.9\text{ }\mu\text{m}$. Helical cone-beam filtered back-projection [30] was used for the reconstruction of the 3D tomographic images. Image visualization was performed using the commercial software Avizo™.

Molecular weight determination was carried out using size exclusion chromatography (SEC). The employed instrument was equipped with a Hewlett-Packard G1362A refractive index (RI) detector and three PLgel $5\text{ }\mu\text{m}$ MIXED-C columns. The instrument was calibrated using polystyrene standards (Agilent Easi Cal) that had molecular weight values ranging from 1 kg mol^{-1} to 200 kg mol^{-1} . A mobile phase of chloroform was used at a temperature of $40\text{ }^{\circ}\text{C}$ and flow rate of 1 mL min^{-1} .

Mass spectrometry data were collected using Electron Spray Ionization (ESI) technique in a LTQ Orbitrap Instrument. Samples were prepared in a solvent mixture of chloroform and acetonitrile.

Proton (^1H) nuclear magnetic resonance (NMR) spectra were obtained at room temperature using a Bruker AV-III 400 MHz NMR spectrometer. NMR solutions were prepared at a concentration of 5 mg mL^{-1} by dissolving samples in deuterated chloroform and spectra were obtained using a Bruker AV-III 400 MHz NMR spectrometer.

2.2.4. Catalyst characterization

Pt/C catalyst was prepared for Transmission Electron Microscope

(TEM) imaging by suspending the sample in ethanol and sonicating it for 15 min. The sample was then deposited on a carbon type B 300 mesh Cu grid purchased from Ted Pella Inc. TEM analysis was performed on an FEI TITAN 80–200 TEM/STEM microscope. Samples were imaged at 200 kV with a typical magnification of 250 – 450 kx.

Fresh and spent Pt/C catalyst was studied using a Rigaku Miniflex 600 benchtop XRD from 10° to 80° 2θ . Recycled catalyst was generated by heating reaction product mixture to $500\text{ }^{\circ}\text{C}$ under 4 % hydrogen flow (balance argon) for 3 h.

3. Results and discussion

3.1. Effects of base hydrophobicity on the hydrothermal dechlorination and catalytic hydrogenation of PVC

Our initial hypothesis was that treatment of PVC in the presence of aqueous base (KOH), hydrogen and a hydrogenation catalyst, would result in the formation of a polyethylene-like molecule. In this reaction scheme, which is shown in Scheme 1, PVC is dechlorinated in an E1cb, E1 or E2 mechanism, forming KCl that is sequestered into the aqueous phase, and a poly-ene molecule, which is hydrogenated by a catalyst.

However, the yields of polyethylene when aqueous inorganic bases are used are very low and independent of the hydrogenation catalyst used (Fig. S6), indicating high reaction selectivity to hydrochar. FTIR analysis of dried reaction product mixture did not identify polyethylene species and identified residual C-Cl bonds indicating incomplete dechlorination. Further, TGA analysis of the product mixture identified residual unconverted PVC (Fig. S7).

We hypothesize that the limited effect of charging the reaction with KOH is attributable to the low partitioning of these types of bases into a polymer phase. We probed this hypothesis with X-ray tomography imaging of reactant and product mixtures using CsOH as an aqueous base and N,N-dimethylhexylamine as an organic base (Fig. 1). Fig. 1 shows orthographic slices (top-down views along the xy plane) of reactant and product mixtures. Both reactant and product mixtures show significant heterogeneity, showing areas of aqueous and organic liquid phases and solid polymers, char and catalyst. More specifically, in the aqueous base samples, the brightest areas represent Cs solution, while lighter grey coloration is representative of Pt particles and PVC (lightest). In the amine samples, PVC and Pt are displayed with higher intensity (more brightly) relative to the aqueous phase because of the low attenuation of water/amine solution. Images of Pt/C catalyst in water and PVC in CsOH solution are shown in Fig. S8 and were used to confirm which particles were PVC and which were Pt/C. The aqueous base images show that after reaction, PVC is not fully converted and maintains particle-like shapes. Images of the amine base samples show that after reaction the PVC is fully converted to char, amine hydrochloride, and hydrocarbon. This is demonstrated by the lack of larger PVC-shaped objects found in the reacted amine sample images, and the formation of amorphous particles containing Pt, char, and polymer.

A volume rendered image of the product mixture from reacting PVC with amine base is also shown in Fig. 1. Brighter colors represent higher attenuating species like Pt catalyst, while lower attenuating darker colored regions contain minimal Pt catalyst. High attenuating Pt species are well dispersed throughout the sample. TEM micrographs and orthographic slices of Pt/C show that the Pt is highly dispersed on the carbon support (Figs. S8 and S9). In the post amine base reaction slice, bright blobs of Pt are observed which are absent in the pre reaction sample. Sintering of Pt catalysts may cause the formation of Pt agglomerates on the micron scale [31].

The tomography results lead us to reformulate the initial hypothesis; we posit that partitioning of the base into the PVC phase is required for dechlorination to take place efficiently. We hypothesized that organic bases, such as alkylamines will partition more effectively into the PVC phase due to their affinity to organic phases and thus would enable rapid dechlorination of PVC and the subsequent catalytic hydrogenation.

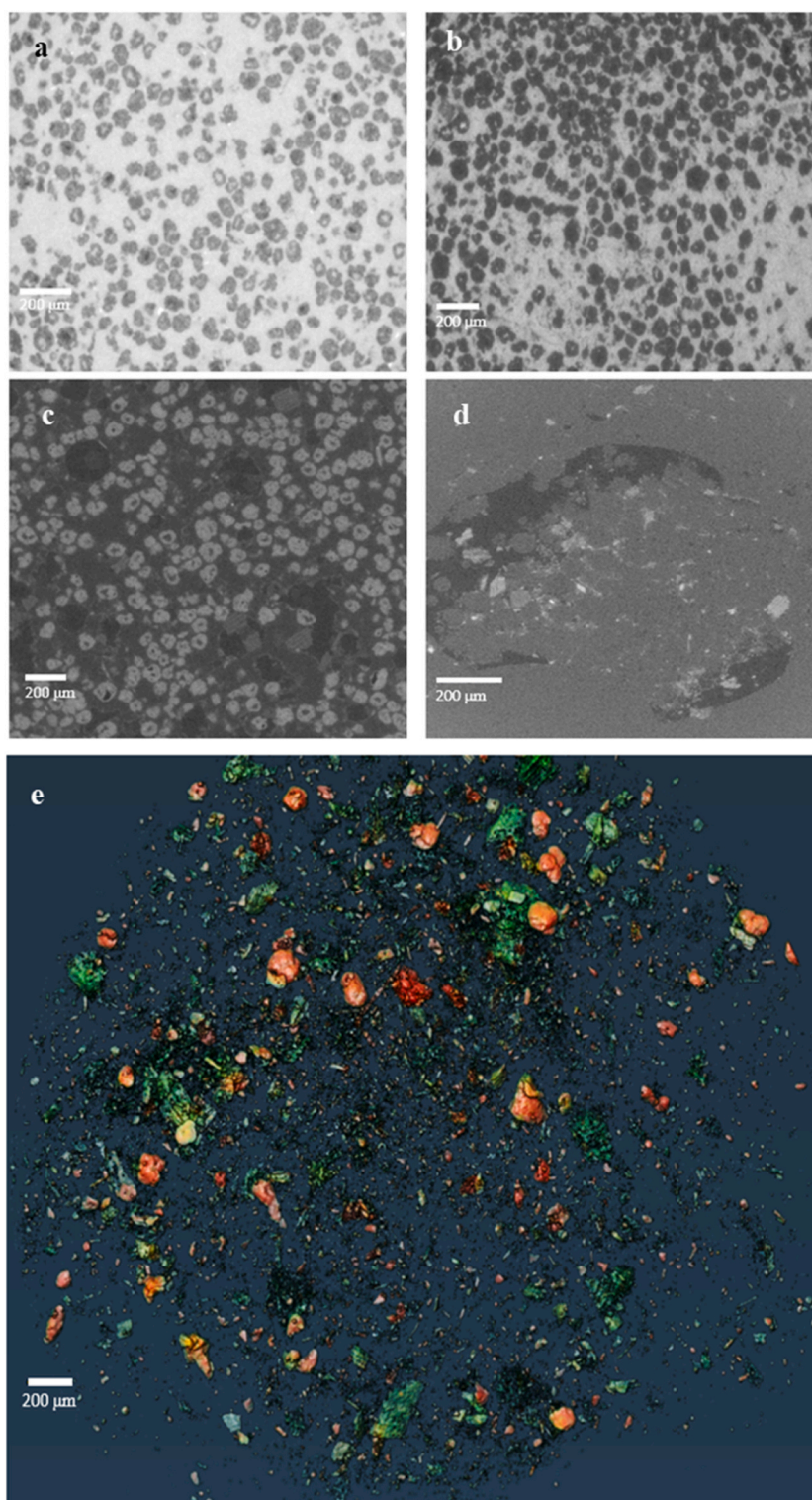


Fig. 1. Tomography images of reactant and product mixtures. (a) Reactant mixture and (b) product mixture from CsOH base samples. The middle row left is (c) reactant mixture and (d) product mixture from N,N-dimethylhexylamine base samples. (e) 3D volume rendered colormap of image (d) Reaction conditions: 24 h, 6.5 bar H_2 , 200 °C, 1:100 Pt:PVC ratio, 2.5 M CsOH solution or 2:1 N:Cl ratio with N,N-dimethylhexylamine base.

Amine bases have previously been reported to accelerate dehydrochlorination of PVC polymers [32].

To probe this hypothesis, we used a range of amine bases in the reaction and quantified the wax yield (Fig. 2). Consistent with our hypothesis, reactions with organic bases dramatically increased the wax yield.

To rationalize the observed effects of alkylamines on increasing wax yields we examined the phase equilibrium of different bases in a PVC/water mixture. At equilibrium, the partitioning of the base between organic PVC particles and aqueous solution can be described by the equality of chemical potentials and fugacities of the base in the aqueous phase and in the polymer phase (Eqs. (S1) and (S2)). Since the activity

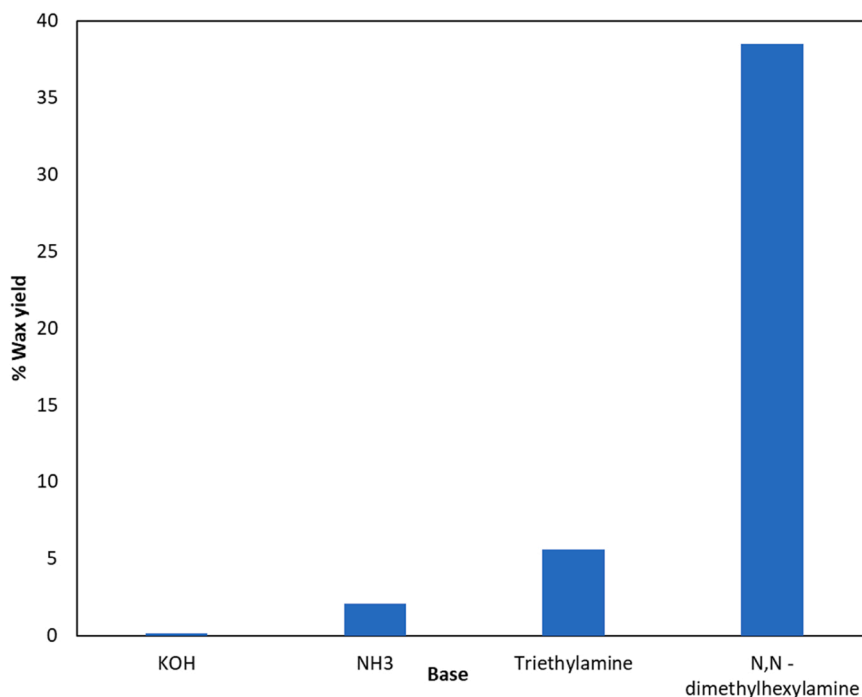


Fig. 2. Base screen for wax yield. Reaction conditions: 24 h, 6.5 bar, H_2 , 200 °C, 1:100 Pt:PVC ratio, 2.5 M KOH solution or 2:1 N:Cl ratio for amine base.

coefficient of a hydroxide ion in a polymer phase is much higher than the activity coefficient of an organic base in the same polymer phase, we can assume that the fraction of amine bases present in the polymer phase will be higher than the fraction of aqueous base in the polymer phase (Eq. (S4)).

However, a direct measurement of the mole fractions of the amines in the PVC and the water phases during reaction is not possible. To address this issue, we assume that the mole fraction of the amine in the PVC phase will be proportional to the octanol water partition coefficient of the amine (Eq. (1)).

$$x_{R_3N}^{pol} \sim K_{ow} = \frac{x_{octanol}}{x_{water}} \quad (1)$$

In this equation, $x_{R_3N}^{pol}$ represents the mol fraction of base in the phase and K_{ow} is the octanol water partition coefficient, which is well tabulated for alkylamine bases [33]. This assumption was probed by quantifying the melt area from DSC analysis of the product matrix, which is a direct indicator of the yield of semi-crystalline polymer obtained from reacting the PVC charge.

Our results demonstrate that increased hydrophobicity of the amine base results in higher product yields. Specifically, the yield of hydrocarbon-like products is approximately linearly dependent on the $\log K_{ow}$ of the amine base (Fig. 3). The increase in yield is attributed to the faster dechlorination of PVC when more hydrophobic amines are used, as shown in Fig. 4. This approach affords almost-quantitative yields of hydrocarbon products when long-chain aliphatic amines such as trihexylamine are used. FTIR spectra of the reaction products show > 99 % dechlorination of the reactant PVC in all cases shown in Fig. 3.

Kinetic curves for PVC dechlorination degree for three amine bases of varying size are shown in Fig. 4. General pathways to dechlorination of organic species such as PVC are catalytic hydrodechlorination, dehydrochlorination, and dechlorination by abstraction of hydrogen generating a leaving mechanism using the alkylamine base [12,34–37]. We see in Fig. 4 that amines with longer alkyl chains increased the rate of dechlorination compared to smaller alkylamines. These results support our rationale that size of the base impacts the rate of dechlorination and overall wax yield, as faster dechlorination leads to a longer residence time for the polyene intermediate.

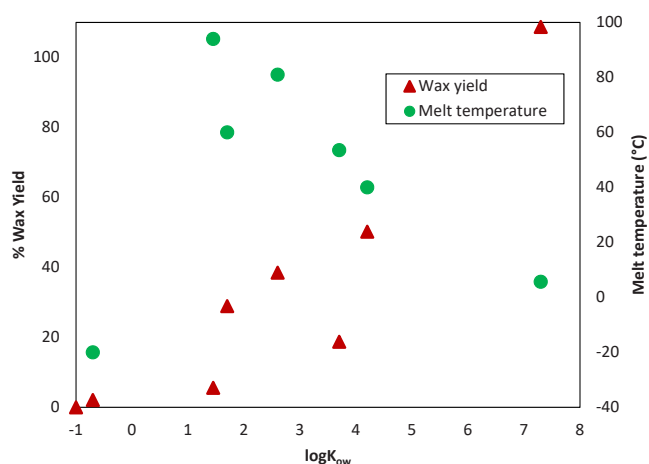


Fig. 3. Amine base screen comparing wax yield and wax melt temperatures. Reaction conditions: 24 h, 6.5 bar H_2 , 200 °C, 1:100 Pt:PVC ratio, 2:1 N:Cl ratio.

While the yield of the reaction is captured by the total melt area, the quality of the wax and its suitability for applications is dependent on its molecular weight. The melting temperatures of the reaction products from reacting PVC with several different alkylamines were close to the temperature ranges of hot melt adhesives (80–130 °C) [29]. The wax melt temperature is shown with the wax yield for reactions with various amine bases (and is typically low at high reaction yields (Fig. 3). Specifically, the highest yield is achieved by reacting PVC with trihexylamine ($K_{ow} = 7.3$). This reaction resulted in a melt temperature of 5 °C, demonstrating significant reduction in molecular weight of the hydrocarbon product and also a non-physical wax yield greater than 100 %. The apparent inconsistency can be explained by the fact that in shorter-chain hydrocarbons (below $M_w = 1000$), the specific enthalpy of fusion (enthalpy of fusion per unit mass) increases as the molecular weight decreases [38,39]. Since the wax yield calibration curve is built with n-docosane wax, products with lower molecular weight will show

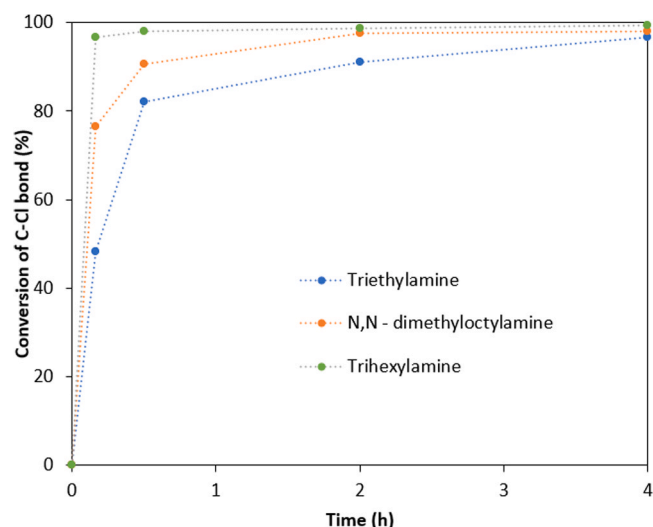


Fig. 4. C-Cl conversion vs reaction time for various sized amine bases. Reaction conditions: 6.5 bar H_2 , 200 °C, 1:100 Pt:PVC ratio, 2:1 N:Cl ratio. Dashed lines serve to guide the eye.

artificially high yields. Particularly in the case of trihexylamine, the melt temperature of the wax roughly corresponds to that of tetradecane, leading to a non-physical yield greater than 100 %.

The decrease in the wax melting temperature can be attributed to the activity of the Pt catalyst for C-C bond cleavage, in addition to the activity for C=C bond hydrogenation. Fig. 5 shows the effects of the catalyst charge on the wax yield. As the catalyst charge in the reactor increases, the wax yield increases, as does the extent of wax hydrogenation. We rationalize this effect as stemming from the C-C bond cleavage activity of the Pt catalyst. Shown in Fig. 5, increasing the catalyst charge increases the yield of the reaction, and also the selectivity to the completely hydrogenated polyethylene-like molecule over the poly-ene intermediate.

However, it is clear from Figs. 3 and 5 that the amines have effects that are not limited to catalyzing the dechlorination and sequestration of the Cl⁻ ions. Specifically, larger amines show lower wax melt temperatures than smaller amines, indicative of more extensive C-C bond scission, for the same wax yield. This observation indicates a solvent effect of these amines onto the polyene intermediate hydrogenation and subsequent hydrogenolysis reactions, an effect demonstrated in past literature [40,41]. Indeed, previous work by Jia et al. [34] demonstrated

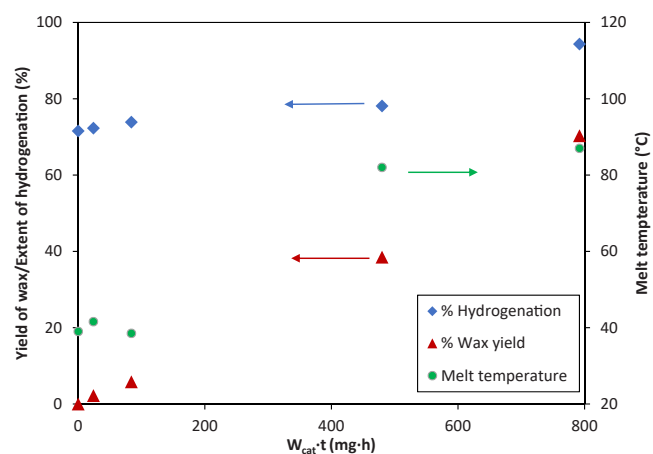


Fig. 5. Catalyst charging vs wax yield, wax melt temperature, and degree of hydrogenation. Reaction conditions: 24 h, 6.5 bar H_2 , 200 °C, 2:1 N:Cl ratio with N,N-dimethylhexylamine base.

that the solvent-induced coiling of polymer macromolecules significantly affected their rate of hydrogenolysis, with linear hydrocarbon solvents allowing access of macromolecules to Ru sites, and more extensive C-C bond scission, a conclusion that is consistent with our observation. In our system, solvent effects may also prevent charring of the intermediate polyene, by preventing coiling and cyclization reactions.

3.2. Effects of reaction conditions

The effects of reaction temperature, pressure, amine concentration, and Pt loading were explored to develop an understanding of the driving forces for converting PVC to hydrocarbon wax. The hydrogen pressure had a positive effect on hydrogenation degree compared to reaction under inert atmosphere (Fig. S10). Increasing hydrogen pressure resulted in a decrease of the gaseous hydrocarbons formed, and an increase in the solids formed, char and wax. (Fig. S11).

Reaction temperatures below 125 °C did not yield quantifiable wax (Fig. S12). Varying the ratio of amine to PVC, shown in Fig. 6 demonstrated a strong effect on reaction outcomes. The maximum in wax yield occurred at an N:Cl ratio of 3 but had a lower melt temperature than the product from reaction with an N:Cl ratio of 2. This is also consistent with our earlier discussion; the increased hydrophobicity of the mixture leads to greater uncoiling, hence more C-C bond scission.

Ammonium hydrochlorides readily form from reacting amine bases with HCl. FTIR analysis demonstrated that > 99 % of the Cl is removed from the wax/char mixture (Figs. S2 and S3). To track the carbon balance the solids yield was measured from combining DSC analysis for obtaining wax yield and TGA analysis for obtaining hydrochar yield. Figs. S6 and S7 show example TGA curves of reacted PVC mixtures, mass loss associated with char was identified at ~ 350 – 450 °C, consistent with mass loss regions for char species [42–44]. Amine mass losses occurred between 50 and 130 °C while amine-HCl masses losses were observed between 100 and 150 °C (Fig. S13).

Weight loss regions from wax product and weight loss regions from char were identified based on literature weight loss regimes for hydrochar and polyethylene wax and TGA curves of solvent extracted wax from the reaction to estimate the fraction of char and wax in the reaction product [44–47]. Fig. 7 shows the yield of wax and solids for experiments at different base concentrations. The solids yield obtained in these reactions shows the reaction produces mainly solids. In the case of the 2:1 N:Cl ratio experiment, gas analysis revealed a 9.4 % yield of gaseous hydrocarbon product demonstrating that some of the unrecovered solids are converted to low molecular weight compounds during reaction. In

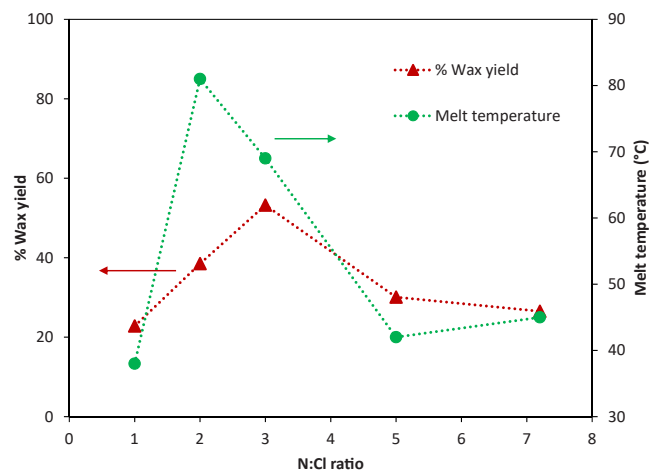


Fig. 6. Varying ratio of amine to PVC. Reaction conditions: 24 h, 6.5 bar H_2 , 200 °C, 1:100 Pt:PVC ratio, N,N-dimethylhexylamine base. Dashed lines serve to guide the eye.

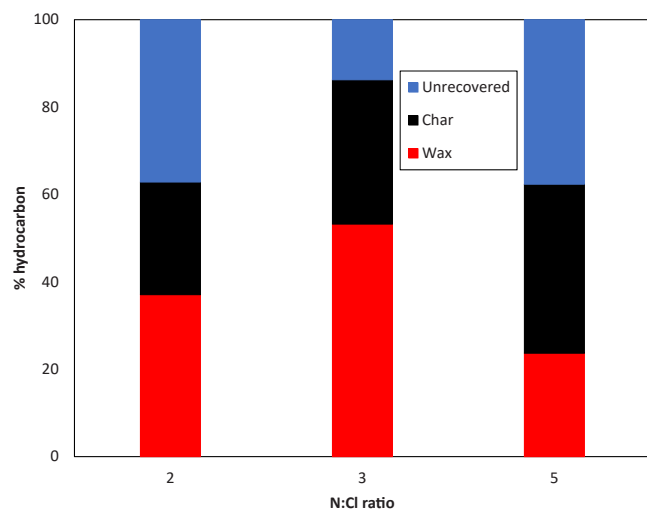


Fig. 7. Recovered hydrocarbon yields vs the ratio of amine to PVC. Reaction conditions: 24 h, 6.5 bar H_2 , 200 °C, 1:100 Pt:PVC ratio, with N,N-dimethylhexylamine base.

addition to the gases identified with GC, some condensed hydrocarbons may be lost in the drying process before analysis with DSC takes place. The observed results in Fig. 4 demonstrate that PVC is effectively dechlorinated with amine bases to a polyene. Reaction selectivity to polyethylene wax is far less than 100 % for most of the amines utilized (Fig. 3), demonstrating that the hydrogenation competes with carbonization of the polyene to hydrochar (Scheme 2). The resultant polyethylene wax has melt temperatures below that of traditional HDPE, which implies that hydrogenolysis readily occurs over the Pt catalyst and leads us to reformulate our idealized reaction (Scheme 1) to include these competitive reactions.

To further characterize product waxes, the waxes were separated from the product mixtures by extraction using xylenes. When evaluated against polystyrene standards, the number-average molecular weight (M_n) of the reactant PVC was determined to be 21.18 kg mol⁻¹ with a polydispersity index of 1.96 (Fig. S14). Moreover, SEC evaluation of the dechlorinated waxes revealed M_n values of 0.25 kg mol⁻¹. Given that relatively low molecular weights were observed for the waxes, further characterization was done using ESI Mass Spectrometry (MS). Here, the waxes were divided into three portions: Samples 1A, 1B and 2 – where sample 1 represents waxes obtained from a 24 h reaction time and sample 2 represents waxes obtained from a 4 h reaction time. Amine impurity was identified in the mass spectrum of all wax samples, however samples extracted at the lower temperature demonstrated lower amine impurity content in the ESI-MS spectra. ESI-MS evaluation of Sample 1B revealed a consistent addition of a + 14 mass-to-charge ratio (m/z) value, which was indicative of repeating $-CH_2$ units (Fig. S15). In

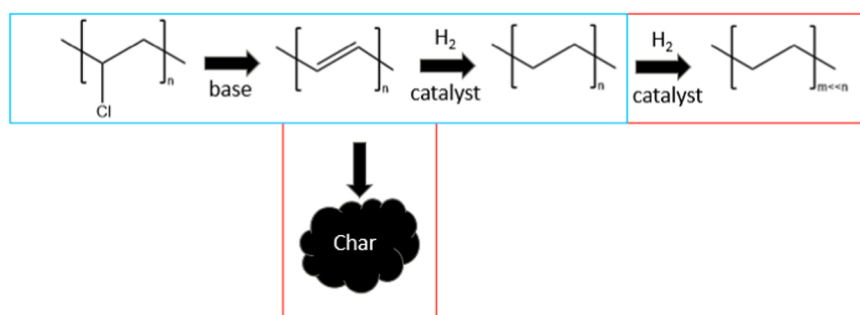
addition, a magnification of weakly resolved fragmentation peaks between m/z values of 350 and 610 (Fig. S16) also revealed a sequential increase of + 42 m/z value, which indicated repeating $(-CH_2)_3$ units. In turn, providing additional credence for polyethylene content in these samples. Sample 1A resembled 1B in the mass spectrum (Fig. S17). ¹H NMR spectra (Fig. S18) collected for Sample 1A showed chemical shifts (0.87 and 1.25 ppm) consistent with polyethylene.

On the other hand, a slightly different trend was obtained for Sample 2 (the dechlorination products that were obtained for a shorter reaction time). Here, fragmentation patterns that were indicative of chlorine presence were observed (Fig. S19). An evaluation of the m/z values between 295 and 440 shows three different pairs of peaks that had a + 2 m/z increase and a 3-to-1 peak height ratio. These arise from Chlorine-35 and Chlorine-37 isotopes which are usually present in percentage abundances of 76 % and 24 % respectively. In addition, the previously described + 42 m/z trend was absent in Sample 2 (Fig. S20), leading to the inference that Sample 2 contains a random mix of chlorinated and non-chlorinated hydrocarbon chains. Thus, a longer reaction time is required to obtain fully dechlorinated waxes.

Reactions with recovered catalyst result in decreased gas and wax yields (Fig. S21). The fresh and recycled catalyst were characterized with XRD; slight sharpening and an increase in the prominence of the peaks were observed in the diffractograms (Fig. S22). TEM image analysis of recycled catalyst (Fig. S23) revealed substantial increases in the particle sizes and the particle size distribution (Fig. S24) showed recycled catalyst particles were larger than fresh catalyst particles. The increased particle sizes in recycled catalyst suggests some sintering may occur during reaction, which may be responsible for the decreased yields in the recyclability experiments.

4. Conclusions

In this work, PVC was selectively converted to wax-like hydrocarbons. This process proceeds in a series reaction, wherein PVC is hydrodechlorinated by an amine base, and the resulting polyene undergoes hydrogenation over a heterogeneous Pt/C catalyst. Increased base hydrophobicity, achieved by increasing the alkyl chain length of the amine base, increases the product yield, a phenomenon attributed to the partitioning of the base into the PVC phase. The hydrogenation of the polyene takes place over the Pt/C catalyst and competes with the hydrogenolysis of the resulting alkane. The presence of the amine bases also influences the overall reaction outcomes by secondary solvent effects. Wax yields greater than 70 % with hydrogenation degrees greater than 90 % were obtained with larger alkylamines such as N,N-dimethylhexylamine and Pt/C catalyst with a Pt:PVC weight ratio of 1:61. The recovered hydrocarbon wax product was appropriate for use as a hot melt adhesive, showing melt temperatures from 60 ° to 90 °C, while the chlorine in the PVC is sequestered as an alkylammonium chloride salt. These results show promise in the development of a process to upcycle PVC to waxes, while recovering Cl, and warrant further study of



Scheme 2. PVC dechlorination with an effective base to form a reactive polyene. Blue boxed area outlines idealized reaction while red boxes outline undesired reactions. The polyene is hydrogenated with hydrogen and a catalyst to form polyethylene or carbonizes to hydrochar. The hydrogenated species may further react to lighter hydrocarbon chains.

catalyst stabilization and regeneration protocols.

CCRediT authorship contribution statement

Scott Svadlenak: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition. **Sophie Wojcik:** Investigation. **Oluwafemi Ogunlalu:** Methodology, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Makayla Vu:** Investigation. **Maoz Dor:** Methodology, Investigation. **Bryan W. Boudouris:** Formal analysis, Resources, Writing – original draft, Writing – review & editing, Supervision. **Dorthe Wildenschild:** Methodology, Software, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualization, Supervision. **Konstantinos A. Goulas:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Konstantinos A. Goulas reports financial support was provided by Vinyl Institute. Scott Svadlenak reports financial support was provided by VentureWell. Konstantinos Goulas reports a relationship with 3M that includes: speaking and lecture fees. Konstantinos Goulas, Scott Svadlenak has patent #US20230012030A1 pending to Oregon State University. Konstantinos A. Goulas, Scott Svadlenak and Sophie Wojcik are considering options for commercialization of this work through a startup company, Renewcat, INC, owned by Konstantinos A. Goulas.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123065](https://doi.org/10.1016/j.apcatb.2023.123065).

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